氏　　名	CHINWANITCHAROEN CHAROEN
学位の種類	博士（学術）
学位記番号	博甲第709号
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学位授与の要件	課程博士（学位規則第4条第1項）
学位授与の題目	PREPARATION AND APPLICATIONS OF ECO-POLYURETHANE:Preparation of Aqueous Polyurethane Dispersions and Deformation Behavior Analysis of Shape-memory Polymer （エコポリウレタンの製造法とその応用：水分散型ポリウレタンの製造と形状記憶ポリマーの変形挙動解析）
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学位論文要旨

要旨

A series of aqueous polyurethane dispersion were prepared by the reaction of hydroxyl-terminated poly(ethylene adipate), dimethylol propionic acid, 4,4'-diphenylmethane diisocyanate, and ethylene glycol. Formation of the dispersion was achieved by phase inversion of an acetone solution of the polyurethane with water, utilizing carboxylate anion groups as the internal emulsifying sites. Formation of the dispersion was achieved by phase inversion or direct emulsification of an acetone solution of the polyurethane with water, utilizing carboxylate anion groups as the internal emulsifying sites. In this work, particle sizes below 100 nm could be formulated for most samples of PU emulsions. The particle size of these PUs were affects by varying the composition, hard segment content, content of ionic site, type of neutralizing agent, and manufacturing method.

In this thesis also explained about shape-memory polymer, it can be concluded that the proposed double-layers model was support for multiphase structure of shape-memory polymer. This could be a basis for molecular design for new type of this smart material.

概要

Polyurethanes have versatility of applications because of their broad range of properties possible. The present thesis focuses on a fundamental knowledge and technology to develop an eco-material from polyurethanes (PUs). There are two parts of works was carried out. Herein, most of content in this thesis, a preparation of aqueous polyurethane dispersions was studied to improve the environmentally benign properties of polyurethanes. Furthermore, an analysis of deformation behavior of shape-memory polymer was simulated to enhance the ability of material design.

In traditional polyurethane coating formulations, solvent have to be used to reduce the viscosity of the coating and to allow its preparation and application by spraying or rolling. The deleterious solvent-based [e.g., *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc)] PUs will be restricted in their traditional applications sooner or later because of the demands of environmental regulations. In

contrast, aqueous PU dispersions would be a candidate with promise to replace the traditional solvent-based PU. Aqueous PU dispersions can be prepared by incorporating ionic groups into the PU backbone. These ionic PUs usually contain pendant acid groups or tertiary amine groups. Water-dispersible anionomer PU is obtained by neutralization of the acid groups. The dispersion of neutralized ionic PU with water results in an aqueous PU dispersion. In the experiments, an aqueous dispersible polyurethane was prepared by the reaction of hydroxyl-terminated poly(ethylene adipate), dimethylol propionic acid, 4,4'-diphenylmethane diisocyanate, and ethylene glycol. Formation of the dispersion was achieved by phase inversion or direct emulsification of an acetone solution of the polyurethane with water, utilizing carboxylate anion groups as the internal emulsifying sites. In this work, particle sizes below 100 nm could be formulated for most samples of PU emulsions.

The particle size of these PUs were affects by varying the composition, hard segment content, content of ionic site, type of neutralizing agent, and manufacturing method as follow:

1. The particle size increased with increasing of hard segment content in PU backbone. The hard segments, however, acted as a filler in block copolymer to serve a high strength and excellence properties of ending products. Thus, the compensation between the properties of ending product control by the hard segment content and the stability of emulsions has to be considered.
2. High content of built-in ionic groups facilitate the dispersity of PU in aqueous medium. It was clearly that the particle size of PU particle decreases when content of ionic group increases. Metal neutralizing agent showed a significant smaller size of particle than amine neutralizing agent.
3. Both phase inversion and direct emulsification can used to produce stable emulsion of PUs. The phase inversion, however, had an advantage over the direct emulsification in a sense of lower energy consumption and the emulsion could be prepared in one reactor that is an important advantage for industry.

The shape-memory and recovery behavior of a shape-memory polymer (SMP) has been investigated numerically. The *double layer model*, as shown in Figure 1, which composed of two non-linear elastic elements, was proposed to describe the behavior of SMP, especially in the shape recovery process.

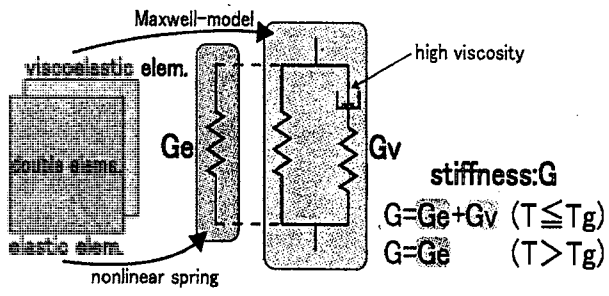

Figure 1 Double layer model for elastomer-type SMP

The proposed double layers model was calculated in plane stress condition using finite element method. The proposed numerical model, double layer model, reveals a good result to predict the shape recovery process for two-dimensional elastomer-type SMP. In this study, the compressive deformation and recovery behavior for compression rates of 10, 50, 65, and 80% of SMP foam were also examined with the change in volumetric compression. From the calculated results, the recovery behavior considerably changes between compression rates of 65 and 80%. Exceeding compression rate of 65%, a property of incompressibility has a large effect on the recovery behavior, possibly since the object was compressed over the volumetric compression region.

学位論文審査結果の要旨

CHINWANITCHAROEN　CHAROEN 氏より提出された学位論文に関して、各審査委員によって個別に審査を行うと共に、平成 17 年 1 月 26 日に開催された口頭発表の結果を踏まえて、同日に論文審査委員会を開催して協議を行った。その結果、以下のように判定した。

ポリウレタンは優れた物性と機能から繊維、塗料、接着剤、合成皮革等の生活に密着した用途に幅広く使用されている。しかしながら現状ではこれらの素材や製品を製造する工程で有害な有機溶剤であるジメチルホルムアミドやジメチルアセトアミドなどが多量に用いられている。氏は脱有機溶剤のひとつのアプローチとしてこれら有害な有機溶剤を用いないポリウレタンの重合処方を検討し、分散性が高く粒子径が制御可能で貯蔵安定性が優れた水分散型機能性ポリウレタンの製造法を開発した。この新規の“グリーンプロセス”は企業からも高く評価され、現在実用化の検討に入っている。一方、氏はポリウレタンの将来の用途のひとつである形状記憶ポリマーの形状付与・形状記憶・復元等の一連の工程での変形挙動を予測できる数値解析モデルを提案し、その予測モデルの有効性を実証した。この予測モデルの開発は、複雑な形状の形状記憶ポリマー構造物の復元時での物体間の干渉問題を事前に回避する方策の提案を可能にした。氏のこれらの研究成果は学会でも高く評価され、プラスチック成形加工学会の秋季大会でベストポスター賞（2003 年）を受賞している。

以上のように、本研究は、学術面のみならず、ポリウレタンの製造の工業化に対する重要で画期的な指針を与え、当該分野に大きく寄与するものである。従って、本論文は博士（学術）の学位に値するものと判断する。

氏　　名	木村　直美
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学位授与の日付	平成17年3月22日
学位授与の要件	課程博士（学位規則第4条第1項）
学位授与の題目	A fate of new and parental macronuclei after conjugation in *Paramecium caudatum*: Developmentally regulated programming by histone modification （ゾウリムシにおける新・旧大核の発生運命とヒストン修飾によるプログラミング）
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論文審査委員（副査）	櫻井　　勝（自然科学研究科・教授），福森　義宏（自然科学研究科・教授），山口　正晃（自然科学研究科・助教授），見上　一幸（宮城教育大学・教授）

学位論文要旨

ABSTRACT

In *Paramecium caudatum*, a parental macronucleus is fragmented into some 40 pieces during conjugation. Microsurgical removal of the new macronucleus during the stages later than the 5th cell cycle produced many clones which regenerated the maternal macronucleus. These clones unexpectedly showed no mating reactivity for about 50 fissions, as if they became sexually immature, implying that 're-programming' of the parental macronucleus did occur. This observation leads us to the assumption that normal 'programming' of the new macronucleus or a reset of aging occurs at this critical period. And then, I demonstrate that the initiation of the parental macronuclear degeneration occurs at about the same fifth cell cycle using acridine orange staining. In addition, to investigate whether histone modification plays a crucial role in the expression of mating reactivity, we treated immature *Paramecium* cells with Trichostatin A (TSA) that is a histone deacetylase inhibitor. Resultant histone hyperacetylation by TSA-treatment leads to a partial recovery of mating reactivity, i.e. the appearance of sexually mature cells, although they were essentially still in immaturity period. This suggests that histone acetylation-methylation is involved in the 'programming' and the subsequent developmental regulation in *Paramecium caudatum*.